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**Title:** Magnetic and electronic properties of disordered (Gd  $1-x$ Yx) 7Pd 3alloys : theoretical study

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# Magnetic and Electronic Properties of Disordered $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$ Alloys — Theoretical Study

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The *ab initio* study of electronic and magnetic properties of  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys are presented. The electronic structure calculations were performed using FP-LAPW method. Basing on the ground-state single-electron results the many particle *s*-*f* model for disordered alloy with strongly correlated band electrons was parameterized. The concentration dependence of the band structure, magnetic moment, and the Curie temperature is presented and discussed in reference to experimental data.

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## 1. Introduction

Recently the crystalline  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys were the subject of intensive experimental studies due to their potential magnetocaloric applications [1–3] (and references cited therein). The Curie temperature ( $T_C$ ) of  $\text{Gd}_7\text{Pd}_3$  compound is too high for magnetocaloric applications but it can be tuned by partial substitution of Gd atoms by non-magnetic Y atoms. In the entire concentration range the  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys crystallize in the  $\text{Th}_7\text{Fe}_3$  structure. Detailed experimental studies of  $\text{Gd}_{7-n}\text{Y}_n\text{Pt}_3$  series revealed several important properties. The Curie temperature was found to decrease nonlinearly with magnetic dilution which has been related to the changes in the electronic structure in the vicinity of the Fermi level. Interpretation of the experimental dc susceptibility with the aid of the Curie–Weiss law have shown that the magnetic moment counted per Gd atom increases with decreasing overall magnetization. The effect has been ascribed to the increment of the local moment of palladium.

To elucidate the microscopic origin of the magnetic properties of  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys we have performed the *ab initio* theoretical investigations of the ground-state electronic and magnetic structure using the supercell approach. In the paper the concentration dependence of local and total magnetic moments, and the band structure in the vicinity of the Fermi level are presented and discussed. Using the simplified formula, based on an approximate solution of the generalized *s*-*f* model [4, 5], the concentration dependence of  $T_C$  is determined and related to the changes of electronic structure at the Fermi level of the alloys.

## 2. Computational procedure

The *ab initio* study of ground-state properties for  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  series were performed using the WIEN2k code [6] based on the full-potential linearized

augmented plane wave (FP-LAPW) method [7]. The electronic states were divided into core states:  $([\text{Kr}]4d^{10})$  for Gd,  $([\text{Ar}]3d^{10})$  for Pd and Y; local orbitals ( $5s$ ,  $5p$  for Gd,  $4s$ ,  $4p$  for Pd and Y) and valence states ( $4f$ ,  $5d$ ,  $6s$  for Gd,  $4d$  for Pd and  $4d$ ,  $5s$  Y). For the core states calculations were fully relativistic while the local orbitals and valence states were calculated using the scalar-relativistic approximation. The exchange-correlation potential (XC) was used in the generalized gradient approximated (GGA) form described in [8]. For the Gd  $4f$  states the enhanced Coulomb correlation term was included applying the GGA+*U* method [9] with the effective  $U_{\text{eff}} = 0.51$  Ry. Atomic muffin-tin spheres radii of Gd and Y was assumed as 2.9 a.u. and for Pd — 2.5 a.u. The *k*-mesh was generated such as to provide approximately 90 *k* points in the irreducible wedge of the Brillouin zone. Sufficient precision of 1 mRy has been reached using the computational parameters  $R_{\text{MT}}K_{\text{MAX}} = 8.0$ ,  $L_{\text{max}} = 10$  and  $G_{\text{max}} = 12$ .

To get rough insight into an effect of changes of the electronic structure at the Fermi level on the  $T_C$  in  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys we have adapted the formula for  $T_C(x)$  derived in [5]. The approach developed in [5] is based on the generalized *s*-*f* model [4] and was used successfully in the description of magnetic properties of  $(\text{Gd}_{1-x}\text{RE}_x)_3\text{Al}_2$  alloys [5]. In order to estimate the  $T_C(x)$  dependence we simplify the relations derived in [5] by neglecting the Coulomb correlation interaction for the itinerant electrons (taken into account approximately in the XC potential used in *ab initio* band structure calculations) and by replacing the mean local susceptibilities of component atoms by their contribution to the density of states at the Fermi level taken from *ab initio* calculations for concentration *x*. With these assumptions the formula for  $T_C(x)$ , applied to  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys, reads

$$T_C(x) = \bar{\chi}_{\text{el}}(1-x) \frac{4}{3} \frac{S_{4f}^{(\text{Gd})}(S_{4f}^{(\text{Gd})} + 1)}{k_B} (J_{\text{Gd}})^2. \quad (1)$$

In Eq. (1),  $S_{4f}^{(\text{Gd})}$  denotes the  $4f$  localized spin of Gd,  $J_{\text{Gd}}$  stands for the coupling constant of *s*-*f* interaction

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at Gd sites and  $\bar{\chi}_{el}$  is the average susceptibility of itinerant electrons, which under assumptions described above takes the form:  $\bar{\chi}_{el} = n_{Gd}[(1-x)\rho_{spd}^{Gd}(\epsilon_F) + x\rho_{spd}^Y(\epsilon_F)] + n_{Pd}\rho_{spd}^{Pd}(\epsilon_F)$ , where  $\rho_{spd}^{Gd,Y,Pd}$  are the atomic ( $s + p + d$ ) densities of states averaged over different crystallographic positions occupied by component atoms for a given concentration  $x$  and  $n_{Gd}$  ( $n_{Pd}$ ) represents the number of Gd (Pd) atoms in stoichiometric  $Gd_7Pd_3$  composition. The  $J_{Gd}$  constant, common for all concentrations, was assumed requiring that the calculated values of  $T_C$  agree qualitatively with the experimental data.

### 3. Calculations and results

All compositions of the  $(Gd_{1-x}Y_x)_7Pd_3$  series crystallize in the hexagonal crystal structure of  $Th_7Fe_3$ -type (space group No. 186). The primitive cell is built of two formula units. Fourteen (Gd, Y) atoms occupy the double 2b sites and two groups of sixfold 6c positions. Six palladium atoms locate at another sixfold-6c group of sites. The lattice parameters and internal atomic coordinates were taken from experiment [1–3]. In simulations of fractional concentration, for each concentration large amount of configurations of yttrium atoms in the supercell would have to be considered. The preparation of unit cell for specified concentration was based on the site preference determined experimentally [2] and on symmetry analysis. Further reduction of number of possible configurations was based on the analysis of calculated formation energies.

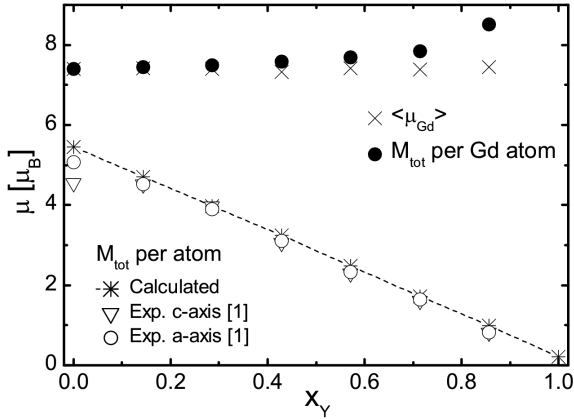


Fig. 1. Local ( $\langle \mu_{Gd} \rangle$ ) and total ( $M_{tot}$ ) magnetic moments as a function of the yttrium concentration compared with experimental data. Presented magnetic data were obtained by averaging over the considered configurations and for  $\mu_{Gd}$  also over internal nonequivalent positions of Gd atoms.

Essential magnetic results are presented in Fig. 1. Besides the stoichiometric  $Gd_7Pd_3$  the calculated total magnetic moment (counted per single atom) follows perfectly the experimental data and falls down linearly according to simple dilution law, but even in the absence of

magnetically active Gd atoms the total magnetic moment persists. Calculations for  $Y_7Pd_3$  compound revealed that the yttrium atoms, with small magnetic moment ( $\approx 0.15 \mu_B$ ), are responsible for non-vanishing magnetic moment of  $Y_7Pd_3$  ( $\mu_{Pd} \approx 0.03 \mu_B$ ). The magnetic results presented in Fig. 1 follow the experimental observation of increasing magnetization counted per single Gd atom. Although the magnitude of the local Gd magnetic moment only slightly oscillates upon alloying ( $\mu_{Gd} = 7.42 \pm 0.03 \mu_B$ ) the calculated total magnetic moment, divided by a number of Gd atom in the structure, increases noticeably for higher concentration of yttrium atoms (Fig. 1). Calculations have shown that in the  $(Gd_{1-x}Y_x)_7Pd_3$  series the palladium atoms are magnetically inactive. The Pd  $4d^{10}$  states hybridize with other valence band states but lying far below the Fermi level cannot be polarized effectively ( $0 < \mu_{Pd} < 0.03 \mu_B$ ). The yttrium magnetic moment is noticeable,  $0.11 < \mu_Y < 0.19 \mu_B$ , and is responsible for the enhancement of the total magnetic moment per Gd atom, estimated from dc susceptibility measurements.

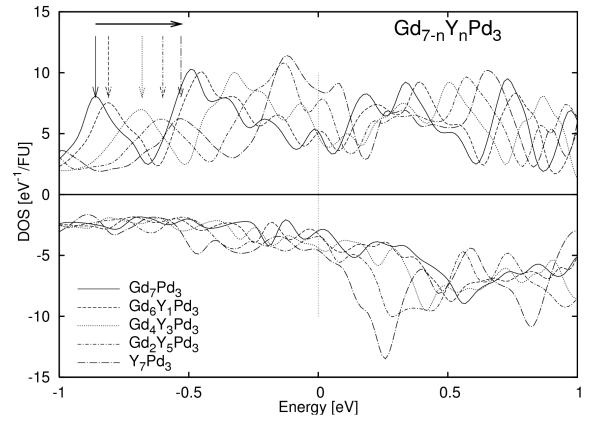


Fig. 2. Detailed picture of changes of density of states near the Fermi level upon alloying. In the figure the energy scale zero is shifted to the Fermi energy (the arrows are explained in the text).

The changes of the band structure, essential for the variation of magnetic and transport properties upon alloying, are restricted to a small energy range near the Fermi energy. Figure 2 shows that some significant changes in the electronic structure can be observed only in the majority spin bands. The minority spin bands change but mainly above the Fermi level. The effect of magnetic dilution on the majority spin bands is the rigid shift of the bands to lower binding energy. The arrows in Fig. 2 are to show the movement of the selected feature of density of states (DOS) upon changes of the yttrium concentration. The shape modification DOS features upon alloying is negligible. The displacement of majority spin bands results in changes of the local atomic densities of states at the Fermi level shown in Fig. 3.

Basing on the partial atomic DOS resulted from *ab initio* calculations (Fig. 3) and using the formula (1), the

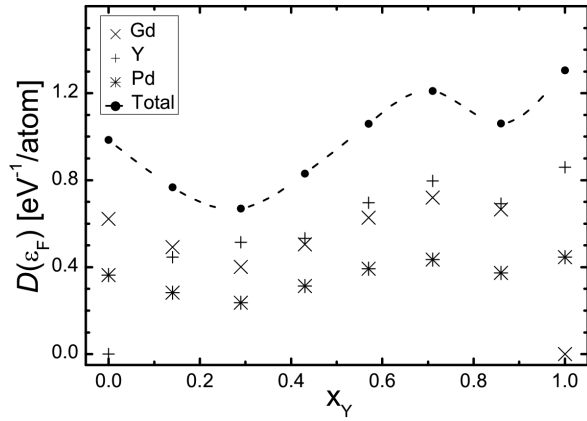


Fig. 3. Local atomic density of states at Fermi level averaged over nonequivalent atomic positions as a function of yttrium concentration in  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$ .

Curie temperature for all considered concentrations was estimated. The estimation of  $T_C$  was performed with the  $s$ - $f$  coupling constant  $J_{\text{Gd}} = 18$  meV, which corresponds, with respect to order of magnitude, to that used in [5] for  $(\text{GdRE})\text{Al}_2$  alloys.

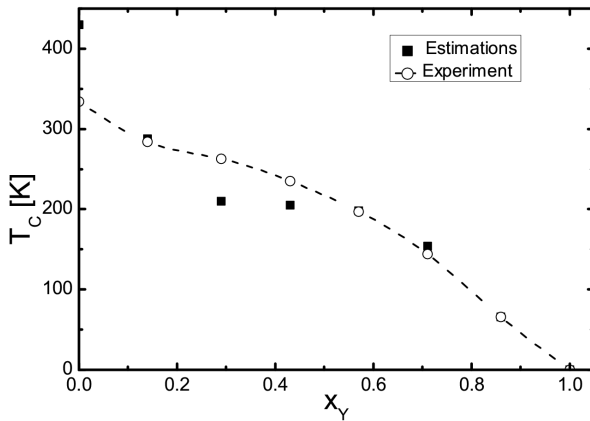


Fig. 4. Estimated Curie temperature  $T_C$  versus yttrium concentration in  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  compared with experimental data [1].

The results of estimations are plotted in Fig. 4 together with experimental values taken from [1]. The simplified model (Eq. (1)) used for the estimation of  $T_C(x)$  dependence reproduces correctly variation of  $T_C$  observed in the range of high yttrium concentration ( $x_Y > 0.5$ ). The worse agreement occurs for higher concentration of gadolinium atoms, which can be due to predominance of the direct exchange coupling of Gd spins over the indirect one generated by  $s$ - $f$  interaction. The biggest discrep-

ancy between experimental and estimated values of  $T_C$  can be seen for stoichiometric  $\text{Gd}_7\text{Pd}_3$  ( $x = 0$ ) where the  $\bar{\chi}_{\text{el}}$  (related to the partial atomic DOS) takes relatively high value.

In summary, calculated dependence of the total magnetic of  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  on yttrium concentration fulfills the simple magnetic dilution law and agrees quantitatively with the experimental data which justifies the supercell approach applied to model the nonstoichiometric compositions. Calculations confirmed the experimental observation of increasing saturation magnetization (per Gd atom) with decreasing concentration of gadolinium. However, according to the *ab initio* results this effect is due to the induced local magnetic of yttrium atoms while Pd atoms are magnetically inactive. The calculated dependence of  $T_C$  on yttrium concentration shows noticeable deviation from linearity and is in qualitative agreement with behavior of  $T_C$  determined experimentally. This indicates significant effect of electronic structure in the vicinity of  $\varepsilon_F$  on magnetic interactions in  $(\text{Gd}_{1-x}\text{Y}_x)_7\text{Pd}_3$  alloys.

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